

# The hydrogen abstraction from a diamond(111) surface in a uniform electric field

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## Abstract

Bond breaking in a strong electric field is shown to arise from a crossing of the ionic and covalent asymptotes. The specific example of hydrogen abstraction from a diamond(111) surface is studied using a cluster model. The addition of nearby atoms in both the parallel and perpendicular direction to the electric field are found to have an effect. It is also shown that the barrier is not only related to the position of the ionic and covalent asymptotes.

## I. INTRODUCTION

Molecular nanotechnology has gained considerable interest in recent years; it's goal is to build complex structures using nanoscale mechanical systems to place (bond) reactive molecules with atomic precision. The work of Drexler [1] gives some idea of what might be possible when atomic level control of matter is achieved. Positional

control has become possible with the development of the scanning tunneling microscope (STM) and atomic force microscope (AFM). Eigler and Schweizer [2] were able to position, with atomic precision, Xe atoms on a Ni surface using an STM tip. However, to be truly useful in molecular manufacturing, the atoms must be chemically bonded in place and the surface probably has to be more stable and less reactive than a metal, as used by Eigler and Schweizer. Therefore it is hard to imagine a first step in the construction of any nanocomponent that does not involve removing one of the surface atoms. This is clearly true for an etching-like process, but it would also be true for adding atoms, where stable surface atoms must be removed to expose a reactive surface in order to add new atoms. One likely surface atom is hydrogen, which is known to tie off the dangling bonds at the surface of carbon or silicon. Removing surface atoms can also be important in macroscopic processes as well. For example, in diamond growth one of the critical steps is removing the H atoms which terminate the growth. Thus there are many reasons to study the selective removal of surface atoms.

Several years ago Musgrave et al. [3] proposed a tool for abstracting a surface hydrogen atom. The disadvantage of this tool is that it must be regenerated after each use. Recently Avouris, Nordlander, and co-workers [4] investigated using an electric field to remove surface adatoms. This approach seems the most practical today for removing surface atoms. Avouris and coworkers identified two mechanisms to explain the bond-breaking process: 1) for weak fields the surface-adatom stretching modes are excited in steps, via multiple-vibrational excitations, until dissociation occurs and 2) for strong electric fields a STM-induced  $\sigma \rightarrow \sigma^*$  excitation causes bond dissociation. The multiple-vibrational excitation process is much slower than bond breaking via STM-induced electronic excitation. They also discussed the second mechanism in terms of mixing of the  $\sigma$  and  $\sigma^*$  orbitals resulting in a bond weakening. They presented potential energy curves that show that, for the correct orientation of

the electric field, the potential becomes increasingly shallow, until it has no well and is completely repulsive.

In this manuscript we present an alternative way to view the rapid dissociation that occurs in a strong field. We avoid a discussion based on orbitals and only consider electronic states, which are physical observables. This approach shows that the field induced dissociation can be viewed as a curve crossing caused by the electric field preferentially lowering the ionic potential relative to the covalent potential.

## II. METHODS

### A. Cluster models

The cluster approach is used to study the abstraction of a hydrogen atom from a hydrogen passivated diamond(111) surface. Carbon atoms at the sides and bottom of the clusters, which are bonding to more distant carbon atoms in the extended system, are bonded to hydrogen atoms. That is, we tie off the dangling bonds with hydrogen atoms. The cluster geometries are optimized in the absence of an electric field and we do not reoptimize them in the presence of the field.

To model the effect of the electric field on the bond between hydrogen and the diamond(111) surface we compute potential energy curves for the C-H dissociation using quantum chemical methods for five different clusters. The simplest cluster contains only one carbon atom,  $\text{CH}_4$  (see Fig. 1). To this cluster we add the next nearest neighbor carbons to obtain  $\text{C}_4\text{H}_{10}$  (see Fig. 1). The  $\text{C}_4\text{H}_{10}$  cluster is extended vertically by adding an extra double-layer to obtain  $\text{C}_{10}\text{H}_{16}$  (see Fig. 1). The  $\text{C}_4\text{H}_{10}$  cluster is also extended horizontally to include the six nearest neighbor on-top sites leading to  $\text{C}_{13}\text{H}_{22}$  (see Fig. 1). Finally the  $\text{C}_{13}\text{H}_{22}$  cluster is extended vertically by adding an extra double-layer to obtain  $\text{C}_{22}\text{H}_{28}$  (see Fig. 1). The smallest cluster,  $\text{CH}_4$ , is used as a model to study the effect of using a restricted versus an unrestricted wave

function both in the absence and in the presence of a uniform electric field. The larger clusters are used to determine the effect of cluster size on the energy barrier for C-H dissociation.

## B. Computational details

All the geometries are fully optimized using the hybrid [6] B3LYP [7] approach, in the absence of a field, in conjunction with the 6-31G\* basis set [8]. For all the clusters, the C-H bond of interest is oriented along the +z axis. The effect of the electric field is studied by adding the electric field to the Hamiltonian and obtaining a new solution. That is, the orbitals are fully optimized in the presence of the electric field. A uniform electric field ( $f$ ) of strength 0.05 atomic units (1 a.u. = 51.4 V/Å) is applied. to the optimized structures along the +z axis parallel to the C-H bond. We compute the potential energy curves as a function of the C-H distance, in the presence and absence of a field, using the 6-31G(d,p), 6-311G(d,p), 6-311++G(d,p), 6-311++G(2d,2p), 6-311++G(2df,2p) and 6-311++G(3df,2p) Pople basis sets [8]. All of the B3LYP calculations are performed using Gaussian94 [9].

To obtain some insight into the effect of the electric field on bond breaking some state-averaged complete-active-space self-consistent-field (SACASSCF) calculations are performed of LiH. The Li 1s orbital is inactive and the Li 2s and H 1s orbitals are active. Two  $^2\Sigma^+$  states, included in the averaging procedure, correlate with the Li+H and Li<sup>+</sup>+H<sup>-</sup> asymptotes. The 6-31G\*\* basis sets are used. These SACASSCF calculations are performed using Molpro96 [10].

### III. RESULTS AND DISCUSSION

#### A. The LiH model

The results of the LiH calculations are shown in Fig. 2. The solid lines correspond to the results obtained without any electric field. The lower curve dissociates to Li+H, while the upper curve dissociates to Li<sup>+</sup>+H<sup>-</sup>. The small hump in the ground state potential is an artifact of the simple level of theory, but the curves are qualitatively correct.

When the electric field ( $f$ ) is added, the energy changes by

$$\Delta E = -\mu f - 1/2\alpha f^2 - \dots,$$

where  $\mu$  is the dipole moment and  $\alpha$  is the polarizability. The dashed lines are the results obtained when an electric field of 0.01 a.u. is added. The ground state is shifted to lower energy and the well depth increases. That is, the electric field stabilizes the molecule more than the atoms, since the atoms do not have any dipole term. The ionic curve undergoes a dramatic change from a bound state potential to an unbound potential. The ionic potential crosses the neutral potential at about 12 Å. The change in the ionic curve arises because the Li<sup>+</sup>+H<sup>-</sup> dipole moment, which for large distances is equal to the separation, and even for a small field, the  $f\mu$  contribution to the energy is very large when the separation between the ions is large.

The effect of increasing the field to 0.02 a.u. is shown in the figure. We note that we have drawn both the adiabatic and approximate diabatic curves to more clearly illustrate the ionic/neutral curve crossing. When the field is added, the neutral diabatic potential is shifted to lower energy and the binding energy is increased. For bond distances greater than about 2 Å, the diabatic ionic potential decreases almost linearly with increasing distance, as expected from the  $\mu f$  term. At shorter  $r$  values, the potential rises rapidly with decreasing bond length due to Pauli repulsion. The adiabatic potentials show that the ground state dissociates to the ionic asymp-

tote. The barrier for this curve crossing dissociation mechanism decreases as the field increases, see the 0.03 a.u. results. Thus if the field is increased to some critical strength, the bond will break and the molecule dissociates.

In our model, dissociation to ions occurs, in this case  $\text{Li}^+$  and  $\text{H}^-$ . It is possible, however, that the H ion would lose the extra electron in the strong electric field. It is clear that the barrier decreases with the electric field strength, it increases with the energy to form the ions (ionization potential (IP) of Li minus the electron affinity (EA) of H), and increases with the strength of the bond to be broken. It also depends on the differences in polarisability between the molecule and atoms, and between the ionic and covalent potentials.

### B. The $\text{CH}_4$ model

We use the  $\text{CH}_4$  model to investigate the best way to model the electric field enhanced hydrogen abstraction at the B3LYP level of theory. The  $\text{H}_3\text{C-H}$  dissociation curves are reported in Fig. 3 and are computed using both spin restricted (R) and unrestricted (U) B3LYP approaches. At short  $r$  the UB3LYP and RB3LYP approaches yield the same solution. As the bond length increases, in the absence of the electric field, the RB3LYP and UB3LYP curves are very different, since the RB3LYP solution dissociates to the ionic limit,  $\text{CH}_3^- + \text{H}^+$ , while the UB3LYP solution dissociates to the ground state systems,  $\text{CH}_3 + \text{H}$ . Clearly a UB3LYP description is necessary to obtain dissociation to the correct asymptote in the absence of the electric field. The computed  $D_e$  of 118.5 kcal/mol obtained using a UB3LYP wave function is in qualitative agreement with the accurate value of 112.2 kcal/mol computed by Partridge and Bauschlicher [5].

In the presence of a strong uniform electric field of strength 0.05 a.u. (2.57 V/Å) oriented along the  $+z$  axis, the  $\text{H}_3\text{C-H}$  dissociation does not occur via a radical pathway, but via an ionic one. The potential curves show a  $1/r$  dependence for a C-H

bond distance greater than 5 Å consistent with an ionic description. For a positive field and a C-H bond oriented along the +z axis, CH<sub>4</sub> dissociates to CH<sub>3</sub><sup>+</sup> + H<sup>-</sup> while for a negative field and a C-H bond oriented along the +z axis, CH<sub>4</sub> dissociates to CH<sub>3</sub><sup>-</sup> + H<sup>+</sup>. The CH<sub>3</sub><sup>-</sup>+H<sup>+</sup> asymptote is much higher in energy than the CH<sub>3</sub><sup>+</sup>+H<sup>-</sup> asymptote because of the large IP of H; as a result, the barrier for C-H dissociation to the CH<sub>3</sub><sup>-</sup>+H<sup>+</sup> asymptote is much larger. Clearly the H<sup>-</sup> asymptote is favored for all clusters considered in this work, therefore we restrict our study to this asymptote for all larger clusters.

While LiH near  $r_e$  and CH<sub>3</sub><sup>+</sup> and H<sup>-</sup> or CH<sub>3</sub><sup>-</sup> and H<sup>+</sup> at infinite separation are clearly well described by a closed shell occupation, the question arises, what does the wave function look like near the barrier to dissociation. As demonstrated in the figure, in the presence of a strong electric field, the UB3LYP and RB3LYP potentials are very similar, with the UB3LYP potentials being slightly lower in energy. That is, the wavefunction is reasonably well described by a closed shell occupation at all  $r$  values. Since the deviations between the UB3LYP and RB3LYP potentials are small we use a RB3LYP wave function for all the remaining calculations, as it is less demanding computationally than the UB3LYP approach.

The effect of basis set improvement on the barrier is summarized in Table I. Expanding the basis set from 6-31G(d,p) to 6-311G(d,p) reduces the barrier by 12 kcal/mol. The population on the dissociating H at the barrier changed from -0.64 using the 6-31G(d,p) basis set to -0.75 using the 6-311G(d,p) basis set. Thus the larger basis set allows more polarization of the charge and stabilizes the ionic component of the bonding and therefore lowers the barrier. Addition of diffuse functions also reduces the barrier as it is able to describe the distortion in the electric field and lowers the ionic potential with respect to the covalent.

### C. Cluster size effects

The barrier clearly depends on the size of the cluster used to model the surface, as the IP of  $\text{CH}_4$  is clearly not that of the surface. In addition, the C-H bond strength is lowered when spectator H atoms are replaced by carbon atoms. Therefore we evaluate the effect of cluster size by systematically extending the  $\text{CH}_4$  model in both a parallel and a perpendicular direction to the field. The following clusters, as shown in Fig. 1, are considered:  $\text{C}_4\text{H}_{10}$ ,  $\text{C}_{10}\text{H}_{16}$ ,  $\text{C}_{13}\text{H}_{22}$  and  $\text{C}_{22}\text{H}_{28}$ .

Before discussing the results, we note a technical problem associated with the larger clusters. While the calculations using the basis sets without diffuse functions are consistent with our expectations, those with diffuse functions yield Mulliken population analyses with charges on the dissociating H that can be greater than 2. It appears that in the strong electric field, there is an energy lowering by moving some electron density from the cluster to the diffuse orbitals on the hydrogen. These solutions do not occur for  $\text{CH}_4$  because of the large IP of  $\text{CH}_3$ . We avoid these solutions by not including diffuse functions in the basis set. Since diffuse functions are expected to lower the barrier, our computed values should be considered as upper bounds.

The energy barriers for a field strength of +0.05 au are summarized in Table I. Since the goal of this expansion is to more accurately model the surface, therefore we compute some additional properties to see if we can correlate their values with the computed barrier. The difference between the ionic and covalent asymptotes should be the IP of the cluster without the hydrogen minus the H electron affinity. The clusters can polarize in the field, and to account for this, we compute the cluster IP in the electric field and the polarisability,  $\alpha$ . We also report the C-H bond strength, without the electric field, since an accurate model of surface should have the correct H-surface bond energy.

The energy barrier drops by more than 50% going from  $\text{CH}_4$  to  $\text{C}_4\text{H}_{10}$ . This is consistent with the weaker C-H bond in  $\text{C}_4\text{H}_{10}$ , a lower IP and a higher polarisability

for  $C_4H_9$ . Adding an extra double-layer to  $C_4H_{10}$  in the direction of the field, to yield  $C_{10}H_{16}$ , reduces the energy barrier by 50%. As the number of layers increases more charge can be polarized towards the hydrogen atom, thus the difference between the IP and IP in the field increases. Extending the  $C_4H_{10}$  cluster perpendicularly to the field, to yield the  $C_{13}H_{22}$  cluster, increases the energy barrier by 30%. The  $C_{13}H_{22}$  cluster is not very polarizable in the direction of the field as indicated by the small difference in the IP with and without the field. On the basis of the IP and of the polarisability, it might have been expected that this cluster would have barrier lower than  $C_4H_{10}$ , but the computed value is larger. The  $C_{22}H_{28}$  cluster allows all the interactions described above to occur. The increase in energy barrier due to the addition of an extra double-layer is counterbalanced by the decrease due to the addition of the surface neighbors. The resulting energy barrier for  $C_{22}H_{28}$  is similar to the one for  $C_4H_{10}$ . The difference between the 6-31G(d,p) and 6-311G(d,p) results decreases as the cluster size increases going from 12.6 kcal/mol for  $CH_4$  to 5.6 kcal/mol for  $C_{22}H_{28}$  as basis set requirements are smaller for larger clusters. Increasing the number of polarization functions by using the 6-311G(3df,2p) basis set reduces the energy barriers by less than 2 kcal/mol.

The results show that the computed barrier is sensitive to the size of the cluster used. The results also show that it is not simply due to changing the IP of the cluster and hence changing the location of the ionic and covalent asymptotes. At the barrier the system still have some covalent bonding character and this is not accounted for by only considering the asymptotes. The polarisability increases going from  $CH_4$  to  $C_{22}H_{28}$  and does not reproduce the trend in the computed barriers. Our results strongly suggest that you must have several nearest neighbors, both in the direction of the field and perpendicular to it. On this basis our  $C_{22}H_{28}$  cluster is probably our best results, however, this cannot be easily demonstrated because of the computational cost of expanding the cluster further. Thus, while it is easy to obtain insight into the

mechanism, it is very difficult to compute quantitative barriers.

#### IV. CONCLUSIONS

In the absence of an electric field the C-H dissociation occurs via a radical pathway. In the presence of a positive electric field the C-H dissociation occurs via an ionic pathway to yield  $R^+ + H^-$ . Cluster size and basis set effects play an important role in the determination of the energy barriers.

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## TABLES

TABLE I. The C-H bond energy, the ionization potential of cluster minus a hydrogen, the same IP but in a uniform electric field, and energy barriers, for the abstraction of hydrogen in a uniform electric field. The used field strength is +0.05 au (2.57 V/Å). The polarisability,  $\alpha$ , is in bohr<sup>3</sup>. All the remaining quantities are in kcal/mol.

Cluster	C-H	IP	IP(f)	$\alpha$	Barrier	
	6-31G*	6-31G*	6-31G*		6-31G(d,p)	6-311G(d,p)
CH <sub>4</sub> <sup>a</sup>	119.3	247.1	254.9	12.71	78.4	65.8
C <sub>4</sub> H <sub>10</sub>	107.4	184.7	188.0	40.94	36.6	26.0
C <sub>10</sub> H <sub>16</sub>	106.4	164.0	185.1	94.86	18.1	10.2
C <sub>13</sub> H <sub>22</sub>	107.3	172.4	172.9	107.48	50.5	43.1
C <sub>22</sub> H <sub>28</sub>	107.5	155.6	163.5	181.15	35.3	29.7

<sup>a</sup> The barriers in the 6-311++G(d,p) and 6-311++G(2df,2p) basis sets are 53.6 and 54.6 kcal/mol.

## FIGURES

FIG. 1. The B3LYP/6-31G\* optimized cluster geometries.

FIG. 2. The SACASSCF potential for LiH as a function of electric field strength. For the 0.02 au field we have drawn approximate diabatic potentials as well as the adiabatic potentials.

FIG. 3. The B3LYP potentials for the dissociation of an H from CH<sub>4</sub> as a function of electric field strength. Both the spin restricted (R) and unrestricted (U) potentials are given.





